Non-Purgeable Volatile Organic Compounds Rapidly Determined by Gas Chromatography/Mass Spectrometry Using Direct Aqueous Injection

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ABSTRACT

A direct aqueous injection (DAI) method was developed for the determination of 18 non-purgeable volatile organic compounds for which no method currently exists. These polar liquids were spiked into distilled water at 1- to 100-ppm levels and analyzed in triplicate using a fused-silica capillary column interfaced to an ion trap mass spectrometer. Using internal standardization, the relative response factors and relative retention times for the 18 compounds were determined. Duplicate data was collected using on-column and splitless injectors. Accuracy and method detection limits (MDLs) were calculated from 10 replicate injections of 2-ppm standards. For splitless injection, the average relative standard deviation (%RSD) for the compounds was 19% and the average MDL was 800 ppb; for on-column injection, the respective values were 13% and 800 ppb. Agreement with EPA-established criteria for 4-bromofluorobenzene will also be shown.

Data from the EMSL-LV Analytical Sciences Division will be presented to show conditions and limitations involving method parameters, such as column type, injection volume, and spectral quality. Attempts to optimize method precision and peak shape will also be discussed.

EXPERIMENTAL

Standard Solutions

Stock solutions were prepared by using a 10-µL syringe to add the neat liquid to distilled water in a 100-mL volumetric flask. The density (Table 1) and volume added were used to calculate the concentration in parts-per-million (ppm). Serial dilutions were prepared in 10-mL volumetric flasks. Triplicate injections at 7 concentrations over a 2-decade range were used to calculate the MDLs and construct response curves.

Conditions

After some initial experimentation, the following conditions were used to collect the data for method development. Two different gas chromatographic columns were used.

GC Conditions

initial temperature	35 °C
initial time	5 min
temperature rate	10 °C/min
final temperature	165 °C
final hold time	2 min
total run time	20 min
transfer line	200 °C

Direct Injection		**Splitless Injection**	
initial temperature	100 °C	temperature	200 °C
initial time	0.1 min	splitless time	30 sec
temperature rate	200 °C/min	split ratio	20:1
final temperature	260 °C		
final hold time	1 min		
total run time	1.9 min		

Mass Spectrometer

scan range	29 to 180 amu
scan time	0.6 sec/scan
mass defect	30 mmu/100 amu
acquire time	17 min

Column #1

dimensions	30 m X 0.53 mm X 1.5 µm film
liquid phase	5% diphenyl-95% dimethyl polysiloxane
head pressure	12 psig
linear velocity	37.5 cm/sec

Column #2

dimensions	30 m X 0.32 mm X 0.25 µm film
liquid phase	Carbowax PEG
head pressure	20 psig
linear velocity	50 cm/sec

In order to match the flow from a wide-bore column to the ion trap vacuum manifold and to facilitate changing columns, a post-column splitter was used (Fig. 1).

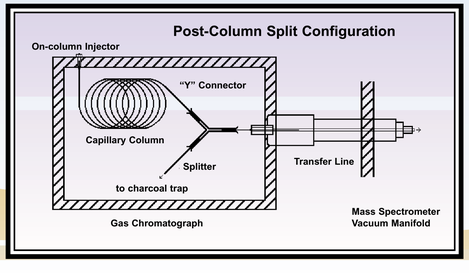


Table Ia. MAGNUM ION TRAP DATA USING SPLITLESS INJECTION

compound	ion m/z	density g/mL	RT min	RRF	%RSD n=21**	MDL ppm
d5-Nitrobenzene IS	82	1.253	16:24	1.000	—	—
Ethanol (1)	45	0.785	1:58	0.106	36.0%	0.88
Acetonitrile (2)	41	0.786	2:12	0.090	32.1%	0.66
2-Propanone (3)	43	0.791	2:14	0.425	15.9%	0.67
Ethyl ether (4)	59	0.714	2:22	0.031	37.1%	1.16
Acrylonitrile (5)	53	0.806	2:32	0.084	10.8%	0.59
1-Propanol (6)	59	0.804	3:01	0.062	17.2%	1.36
Propionitrile (7)	54	0.772	3:20	0.159	14.7%	1.36
2-Butanone (8)	43	0.805	3:43	0.540	20.3%	0.58
Ethyl Acetate (9)	43	0.902	4:13	0.764	25.1%	0.58
Butanol (iso+n) (10)	56	0.805	5:49	0.201	11.2%	0.89
3-Pentanone (11)	56	0.814	6:53	0.488	12.4%	0.65
p-Dioxane (12)	88	1.034	7:13	0.189	25.6%	0.54
Methyl methacrylate (13)	69	0.936	7:25	0.267	21.7%	0.55
4-Methyl-2-pentanone (14)	43	0.800	8:16	0.874	5.9%	0.68
Ethyl methacrylate (15)	69	1.100	9:38	0.554	11.1%	0.39
2-Hexanone (16)	43	0.812	9:42	1.052	6.3%	0.76
3-Picoline (17)	93	0.957	11:34	0.745	13.6%	1.04
1,3-Dichloro-2-propanol (18)	79	1.351	12:22	0.351	24.4%	1.18

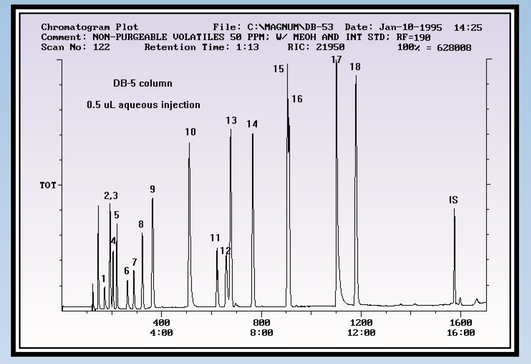
Table IIIb. SATURN ION TRAP DATA USING ON-COLUMN INJECTION

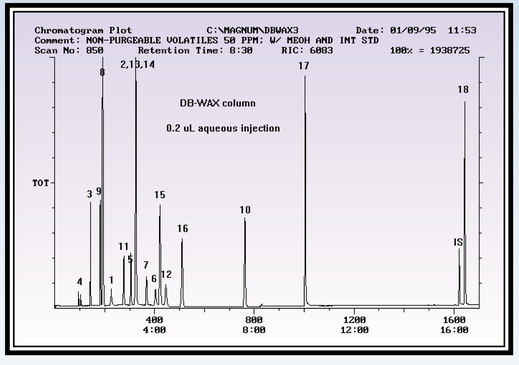
compound	ion m/z	density g/mL	RT min	RRF	%RSD n=21**	MDL ppm
d5-Nitrobenzene (IS)	82	1.253	16.19	1.000	—	—
Ethanol (1)	45	0.785	1.89	0.126	27.4%	1.65
Acetonitrile (2)	41	0.786	2.11	0.144	14.6%	0.88
2-Propanone (3)	43	0.791	2.13	0.465	5.7%	0.34
Ethyl ether (4)	59	0.714	2.25	0.055	11.6%	0.70
Acrylonitrile (5)	53	0.806	2.42	0.062	16.5%	0.99
1-Propanol (6)	59	0.804	2.90	0.054	18.7%	1.13
Propionitrile (7)	54	0.772	3.17	0.146	13.9%	0.84
2-Butanone (8)	43	0.805	3.55	0.616	5.1%	0.31
Ethyl Acetate (9)	43	0.902	3.99	0.811	8.7%	0.52
Butanol (iso+n) (10)	56	0.805	5.60	0.126	8.7%	0.52
3-Pentanone (11)	56	0.814	6.64	0.443	22.2%	1.34
p-Dioxane (12)	88	1.034	7.00	0.218	25.2%	1.52
Methyl methacrylate (13)	69	0.936	7.16	0.270	22.8%	1.38
4-Methyl-2-pentanone (14)	43	0.800	8.03	0.836	7.6%	0.46
Ethyl methacrylate (15)	69	1.100	9.40	0.567	4.0%	0.24
2-Hexanone (16)	43	0.812	9.47	1.020	5.8%	0.35
3-Picoline (17)	93	0.957	11.41	0.405	12.0%	0.72
1,3-Dichloro-2-propanol (18)	79	1.351	12.19	0.419	9.3%	0.56

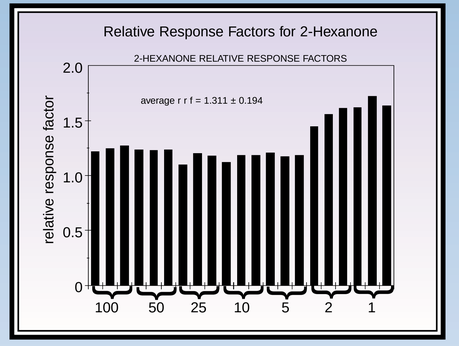
**Triplicate injections at 7 concentration levels over a 2-decade range.

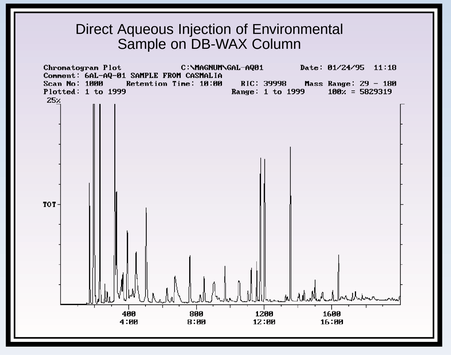
Table II. 4-Bromofluorobenzene tune criteria in aqueous injections.

4-BFB mass	Method 524	Method 8240b	DAI average	%rsd*
50	8 to 40% of mass 95	15 to 40% of mass 95	22	4
75	30 to 66% of mass 95	30 to 65% of mass 95	56	2
95	base peak, 100%	base peak, 100%	100	30
96	5 to 9% of mass 95	5 to 9% of mass 95	6	2
173	less than 2% of mass 174	less than 2% of mass 174	0	—
174	50 to 120% of mass 95	greater than 50% of mass 95	70	3
175	4 to 9% of mass 174	5 to 9% of mass 174	8	1
176	93 to 101% of mass 174	95 to <101% of mass 174	101	1









CONCLUSIONS

1) DAI method showed good chromatographic separation on a two columns of different dimensions and liquid phases.
2) Adequate sensitivity was obtained for non-purgeable volatiles.
3) DAI is rapid, easily applied, and generates no waste solvent.
4) This research and previous work show that direct aqueous injection is feasible for these compounds with a variety of columns, injectors, injection volumes, and instruments.